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Thermodynamic and Hydrodynamic Properties of Dilute Solutions of Cyclic and Linear Polystyrenes

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ABSTRACT: The thermodynamic and hydrodynamic properties of cyclic and linear polystyrenes, ranging from 10 000 to 180 000 molecular weight, in dilute solutions of cyclohexane have been measured by small-angle neutron scattering (SANS) and dynamic light scattering. The diffusion coefficient $D(c)$ was measured at $\theta_{A_2=0}$ as a function of concentration c . The hydrodynamic radii were determined and found to be slightly smaller for cyclic than for linear macromolecules. The slope k_D , defined by $D(c) = D(0)(1 + k_D c)$, was found to be negative and was, within experimental error, independent of molecular architecture. The molecular weight dependence of the radius of gyration, the hydrodynamic radius, and k_D is discussed.

1. Introduction

Macroscopic polymers as well as other model macromolecules have been a fascinating curiosity for theoreticians and chemists. Recently, model polymers such as cycles, stars, and combs have found renewed interest in testing theories that have been developed to model the flow behavior of molten polymers from a molecular point of view.^{1,2} Structure-property relations in the melt state, as well as in dilute solution (single chain), of model macromolecules can help to test the theoretical predictions and ultimately to understand the behavior of macromolecules. The theoretical aspects of the conformation of ring polymers have been studied since the 1940s.⁴⁻⁶ The discovery of DNA macromolecular rings in living cells in the early 1960s,⁷⁻⁹ together with the controlled chemical synthesis of well-defined cyclic macromolecules such as poly(dimethylsiloxane)^{10,11} and polystyrene,¹²⁻¹⁸ made possible a systematic investigation of the theoretical predictions by experiments. A first-order characterization of cyclic macromolecules was performed by using size exclusion chromatography and viscometry in dilute solution.¹⁰⁻¹⁸ A more detailed characterization of conformational statistics, molecular dimensions, and dynamical properties in dilute solution may be obtained with small-angle neutron scattering and quasi-elastic light scattering or neutron scattering. Studies of cyclic and linear poly(dimethylsiloxanes) in deuterated benzene¹⁹ have shown that the theoretically predicted^{4,5,20,21} ratio $\langle R_g^2 \rangle_c / \langle R_g^2 \rangle_L = 0.5$ for Θ -solvent and 0.526 for good solvent is in good agreement with the experimental results. Neutron scattering studies of cyclic polystyrene in deuterated toluene (good solvent)²³ and deuterated cyclohexane²⁴ were reported earlier. Here, we give a more detailed account of the results for a relatively broad molecular weight range.

The diffusion of linear and cyclic poly(dimethylsiloxanes) in dilute solution has been measured by quasi-elastic neutron scattering²⁵ and light scattering.^{26,27} The diffusional properties of cyclic polystyrenes were studied by sedimentation velocity, where it was found that the sedimentation and intrinsic viscosity measurements were

mutually consistent.²⁸ Here, we report the diffusional properties in dilute solution of cyclic polystyrenes measured by quasi-elastic light scattering.

2. Experimental Section

The synthesis and characterization of the specimens investigated in this work were presented previously.^{12,17,29} Five samples of cyclic polystyrenes (PSC1-PSC5) and their corresponding linear precursors (PSL1-PSL5) in the molecular weight range 11 500 $\leq M < 181\,000$ were studied.

Small-Angle Neutron Scattering Measurements. The polystyrenes were dissolved in deuterated cyclohexane (C_6D_{12}) with a degree of deuteration $>99\%$, as purchased from Aldrich. Four solutions of each specimen were made equally spaced, up to 4% (w/v) for molecular weights $<80\,000$ and up to 2% (w/v) for higher ones. Determination of $\theta_{A_2=0}$ by light scattering was reported previously for samples of cyclic polystyrenes of similar molecular weights.^{28,29} In these studies, $\theta_{A_2=0}$ was independent of the molecular weight in the range of investigation. The neutron scattering measurements were performed at 33 and 40 °C, at which the second virial coefficients A_2 are zero for cyclic and linear polystyrene, respectively. It should be noted that these temperatures differ by about 5 °C from the $\theta_{A_2=0}$ for cyclic and linear polystyrenes in hydrogenated cyclohexane. As demonstrated long ago by Strazielle and Benoit,³³ this difference is due to the deuterium effect. The National Bureau of Standards small-angle neutron scattering facility was used for the measurements. Quartz cells of 2-mm thickness were used, and the primary beam had a cross section between 0.5 and 1.5 cm². The scattering vector range was $0.015 < q \text{ (Å}^{-1}\text{)} < 0.15$, where $q = (4\pi/\lambda) \sin(\theta/2)$ (λ is the neutron wavelength and θ is the scattering angle). Absolute intensity measurements were made against a silica secondary standard specimen.³⁰

Quasi-Elastic Light Scattering Measurements. The quasi-elastic light scattering experiments of dilute solutions of cyclic and linear polystyrenes in hydrogenated cyclohexane at 28 and 35 °C, respectively, were performed with a 128-channel correlator (Brookhaven Instruments 200SM) and an automatic goniometer set at 45° to obtain the correlation function $C(t)$. Two samples, PSC3 and PSL4', were measured at several angles (20°, 30°, 45°, 60°, and 75°) and gave nearly identical results at all angles with a standard deviation of $<1\%$ in the first cumulant Γ . The sample time was chosen as follows:

$$\Delta t = \frac{2}{m}(\Gamma^{-1}) \quad (1)$$

where m is the number of channels, 128. Six runs of 50-100-s duration were measured for each concentration c . The sample

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Table I
Molecular Characteristics of Linear (PSLX) and Cyclic (PSCX) Polystyrene Macromolecules^a

		M_w WALS	M_w SANS	$\frac{M_w}{M_n}$	$10^7 D_0$	$-k_D^C$	$\langle R_h \rangle (\text{\AA})$ ± 0.5 LS	$\frac{\langle R_h \rangle_C}{\langle R_h \rangle_L}$ ± 0.05	$\langle R_g \rangle (\text{\AA})$ ± 1.0 SANS	$\langle R_g \rangle (\text{\AA})$ corr ± 1.0	$\frac{\langle R_g \rangle_C^2}{\langle R_g \rangle_L^2}$ ± 0.05	$\frac{\langle R_g \rangle}{\langle R_h \rangle}$
PSL1	▲	10500	11200	1.15	11.50	6.17	26.1	0.96	31.0	29.6	0.50	1.19
PSC1	△	11100	12400	1.09	11.91	6.88	25.2		22.0	21.5		0.87
PSL st	■	28000		1.04	8.00	7.88	37.6	0.87			0.51	
PSL2	■	27200	27300	1.10	7.36	9.38	40.8		47.0	45.5		1.15
PSC2	□	28600	27000	1.05	8.46	7.68	35.5	0.83	33.5	33.0	0.50	0.94
PSL3	▼	45000	46100	1.19	6.01	10.15	50.0		62.0	58.6		1.24
PSC3	▽	42000	45000	1.10	7.22	9.28	41.6	0.92	44.0	42.6	0.50	1.06
PSL4	◆	79500	80300	1.10	4.87	16.84	61.7		77.5	75.0		1.25
PSL4'	◈	81000		1.05	4.84	14.43	62.1	0.92			0.50	
PSC4	◇	79400	79500	1.12	5.27	12.52	57.1		55.0	53.0		0.96
PSL st	●	110000		1.05	3.93	15.78	76.5	(0.90)			(0.50)	
PSL st	●	233000		1.05	2.69	30.48	111.8					
PSC5	○	181500		1.10	3.67	23.16	81.9		(84.3)			

^a PSL st: Pressure Chemical Co. standard polystyrenes. PSL4: linear polystyrene from duplicate synthesis of PSL4.

was illuminated with a He-Ne 124B laser, and the count rate varied from 50 000 to 300 000 s⁻¹. The correlation function was fit by the method of cumulants

$$\ln \left(\frac{C(t)}{B} - 1 \right)^{1/2} = \ln b^{1/2} - \Gamma t + \mu_2 t^2 / 2 + \dots \quad (2)$$

truncating after the third term, B being the base line. For the calculations, we used a measured base-line value that was the average of the four delay channels 1029–1032 times the sample time Δt . The measured and calculated base line agreed within 0.05% for all runs. The parameter b in eq 2 is an optical constant.

The normalized second cumulant μ_2/Γ^2 was 0.05 ± 0.03 for all except PSC1 and PSL1, where it was 0.3 and 0.15, respectively.

3. Results and Discussion

Small-Angle Neutron Scattering. Radii of gyration, molecular weights, and second virial coefficients A_2 were determined by the Zimm plot type of analysis.³¹ The z average of the mean square radius of gyration, $\langle R_g^2 \rangle_z$, and the weight average of the molecular weight, M_w , are presented in Table I. Also presented are the corrected values of the mean square radius of gyration, $\langle R_g^2 \rangle_{\text{corr}}$, which corresponds to a monomolecular polymer coil with the same molecular weight. The above correction was performed by using Oberthür's treatment,³⁴ which assumes a Schultz distribution function.

$$\langle R_g^2 \rangle_{\text{corr}} = \langle R_g^2 \rangle_z \frac{1 + u\Gamma(1/u + 3)}{1 + 2u\Gamma(1/u + 2 + \alpha)} \left(\frac{1}{u} + 1 \right)^{\alpha-1} \quad (3)$$

where $u = M_w/M_n - 1$ (M_w/M_n was determined by size

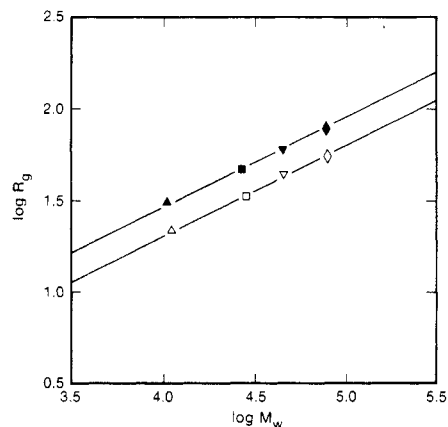


Figure 1. Molecular weight dependence of the radius of gyration for cycles (△, □, ▽, ◇) and their corresponding linear precursors (▲, ■, ▼, ◆).

exclusion chromatography), α is the exponent of the Equation $\langle R^2 \rangle_z = KM_w^\alpha$, and $\Gamma(y)$ is the gamma function.

Figure 1 shows the molecular weight dependence of the radii of gyration of the cycles and their corresponding linear precursors. The power law dependence of the dimensions as a function of the molecular weight is 0.5 for both classes of macromolecules. The absolute dimensions of the cycles are smaller by approximately 30%—in agreement with the theoretical prediction,^{4,5,20} which states that

$$\langle R_g^2 \rangle_{\text{cycles}} / \langle R_g^2 \rangle_{\text{linear}} = 0.5 \quad (4)$$

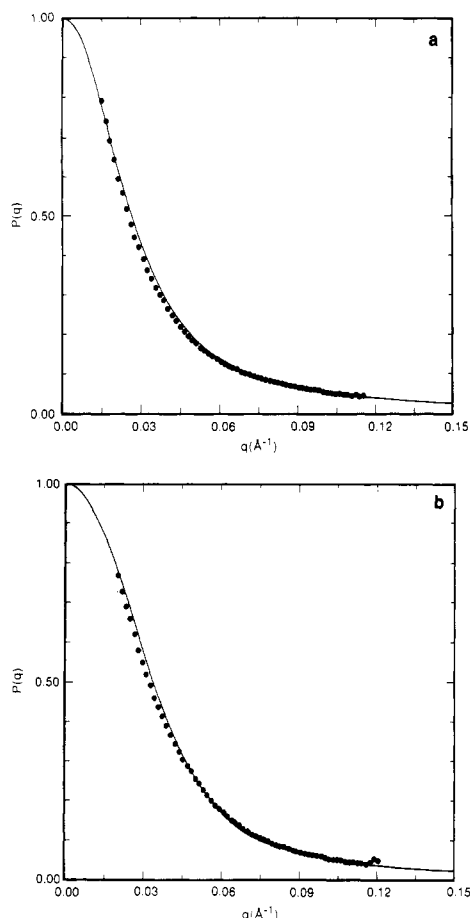


Figure 2. (a) Scattering function for a linear polystyrene (PSL3): experimental data and theoretical prediction after Debye's scattering function. (b) Scattering function for a cyclic polystyrene (PSC3): experimental data and theoretical prediction after Casassa's scattering function for cyclic macromolecules.

The measured particle scattering functions were compared with the Debye function

$$P_L(u) = \frac{2}{u^4}(u^2 - 1 + e^{-u^2}) \quad (5)$$

for the linear precursors and the Casassa function⁵

$$P_C(u) = (2/u^{1/2})e^{-u/4} \int_0^{u^{1/2}/2} e^{t^2} dt \quad (6)$$

for the cyclic molecules, where $u = R_g q$. As an example, Figure 2 presents the observed scattering for PSL3 and PSC3. It demonstrates that the experimental results and the theoretical predictions are in good agreement. A representation that shows the difference in scattering behavior between a cyclic and a linear macromolecule more clearly is $q^2 P(q)$ vs. q (Figure 3). The maximum at intermediate angles observed for the cyclic polymer is due to the higher segment density of the cyclic macromolecules. At larger angles, the same limit is approached, since then it is no longer possible to observe whether a segment belongs to a cyclic or a linear macromolecule. However, the asymptotic behavior of the experimental data for the cyclic polystyrene tends to deviate from the theoretical prediction. This could be due to either chain stiffness^{46,47} or topological constraints^{45,48} or both. Further experiments are under way to evaluate these contributions.

Quasi-Elastic Light Scattering Measurements. The mutual diffusion coefficients at concentration c , $D(c)$, for all cyclic and corresponding linear homologues are presented in Figure 4. Four or more values of $D(c)$ obtained at different concentrations were extrapolated to infinite

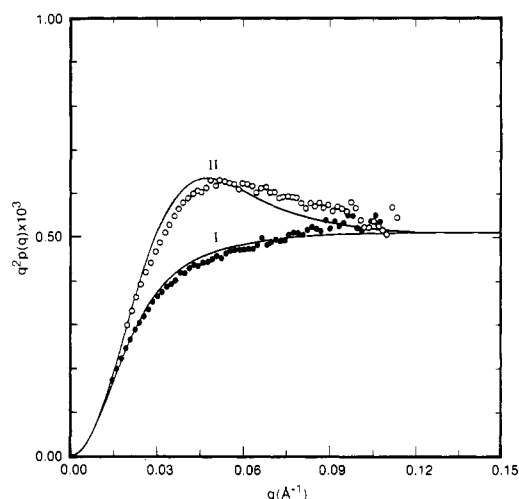


Figure 3. Asymptotic behavior of the particle scattering function of (I) a linear polystyrene (PSL3) and (II) a cyclic polystyrene (PSC3).

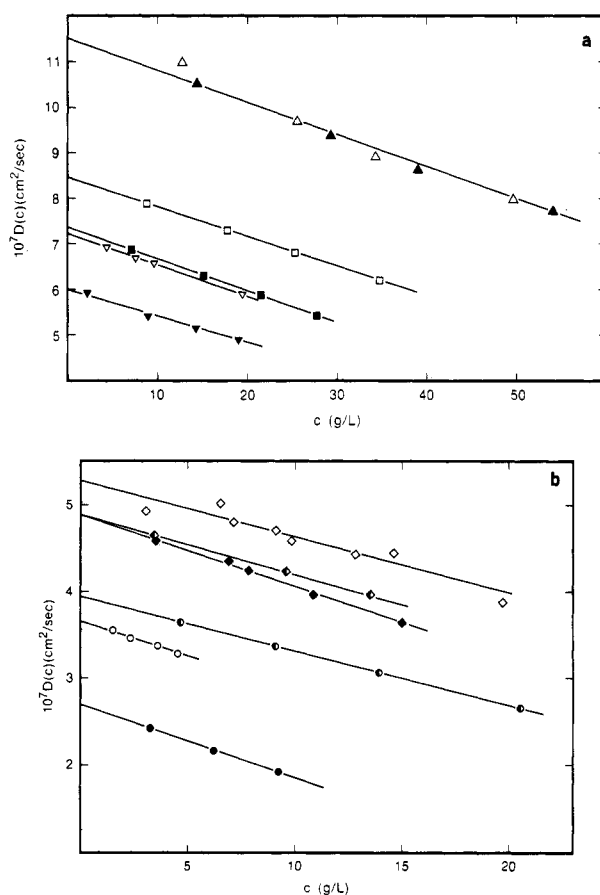


Figure 4. Diffusion coefficients of linear (filled symbols) and cyclic (open symbols) polystyrenes in cyclohexane at $\theta_{A_2}=0$ for several molecular weights.

dilution to obtain $D(0)$ (Table I). The hydrodynamic radii R_h of these cyclic and linear macromolecules were calculated from the well-known Stokes-Einstein relation for diffusion

$$R_h = \frac{k_B T}{6\pi\eta_0 D(0)} \quad (7)$$

where k_B is Boltzmann's constant, T is the absolute temperature, and η_0 is the viscosity of the solvent. The values of R_h are reported in Table I, and their molecular weight dependence was found to be $R_{h,L} = (0.227 \pm 0.005) M_{w,L}^{0.50 \pm 0.01}$ and $R_{h,C} = (0.202 \pm 0.005) M_{w,C}^{0.50 \pm 0.01}$ (see

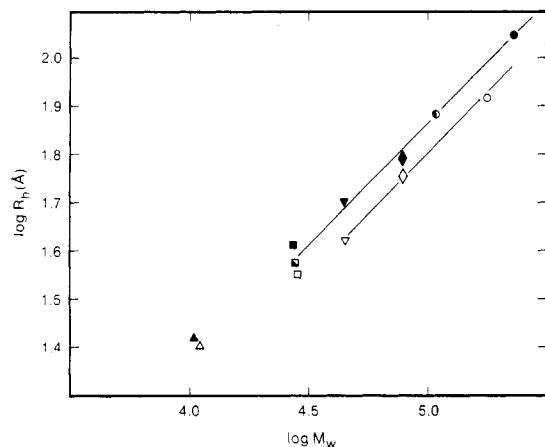


Figure 5. Molecular weight dependence of the hydrodynamic radius for the cycles (open symbols) and their corresponding lines (filled and half-filled symbols).

Figure 5), with R_h in angstroms. The two lowest molecular weights were eliminated from the linear regression to obtain these relations for both the linear and cyclic samples. The ratio of R_h of the linear samples to that of the cyclic samples $R_{h,L}/R_{h,C} = 1.12 \pm 0.06$, which is in reasonable agreement with the first-order perturbation prediction of 1.178 using the Kirkwood equation in the limit of infinite hydrodynamic interaction.³⁵⁻³⁷ As expected, the hydrodynamic radius is less sensitive to the ring geometry than either the mean square radius of gyration or the intrinsic viscosity. The relation obtained for linear polystyrene is in excellent agreement with $R_{h,L} = 0.229M_w^{0.50}$ reported recently on the basis of several independent investigations covering a much broader molecular weight range.³⁸ The deviation of R_h (or $D(0)$) from the power law relations given above at molecular weights $M \lesssim 30\,000$ has been observed previously, where it was suggested that both a more exact treatment of the hydrodynamic interaction and consideration of chain stiffness are needed to interpret behavior in this low molecular weight region.³⁹

As has been observed in several studies on linear polymers with no excluded volume effects, the concentration dependence of the mutual diffusion coefficient, $\partial D(c)/\partial c$, was negative and independent of molecular weight.⁴⁰ Expanding the diffusion coefficient in powers of the concentration c

$$D(c) = D_0(1 + k_D c + \dots) \quad (8)$$

permits the expression of the concentration dependence of $D(c)$ in terms of k_D for comparison with theoretical predictions. At finite concentrations, $D(c)$ is influenced by both thermodynamic and hydrodynamic interaction among chain segments, as is clearly seen in the relation between $D(c)$ and the friction coefficient $f(c)$:

$$D(c) = \frac{kT}{f(c)}(1 - \bar{v}c)(1 + 2A_2Mc + \dots) \quad (9)$$

where $f(c)$ may also be expanded in powers of c

$$f(c) = f_0(1 + k_f c + \dots) \quad (10)$$

so that

$$k_D = 2A_2M - \bar{v} - k_f \quad (11)$$

where \bar{v} is the partial specific volume of the polymer in the solvent. Since k_f is always positive, when $A_2 = 0$, k_D is expected to be negative as observed here. In good solvents, where the A_2M term becomes large, k_D is positive and increases with M . The dependence of k_D on M for linear and cyclic polystyrene in cyclohexane and in the good solvent tetrahydrofuran (data of Duval et al.³²) is shown

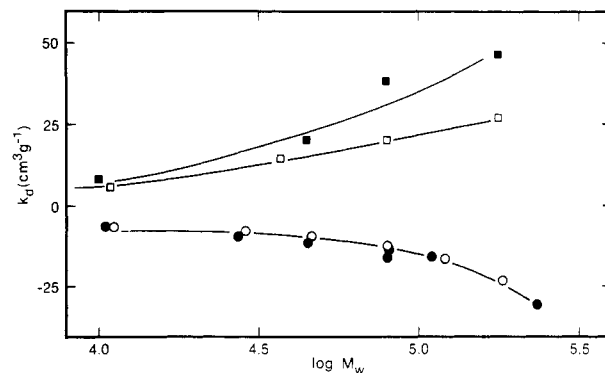


Figure 6. Molecular weight dependence of k_D for cycles (○, □) and their corresponding lines (●, ■) at $\Theta_{A_2=0}$ (●, ○) and in the good solvent (■, □) THF at 25 °C.

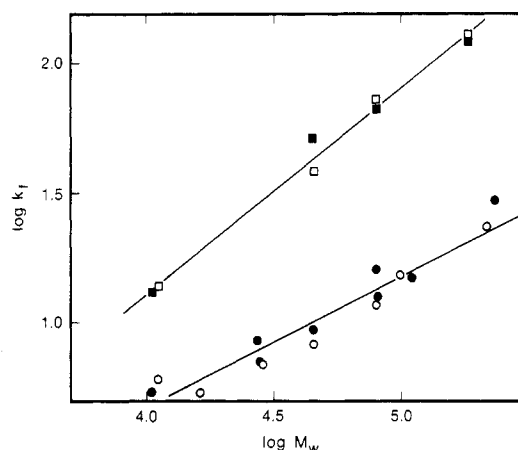


Figure 7. Molecular weight dependence of k_f for cycles (○, □) and their corresponding lines (●, ■) at $\Theta_{A_2=0}$ (●, ○) and in the good solvent (■, □) THF at 25 °C.

in Figure 6. In cyclohexane at the Θ -temperature (28 and 35 °C for the cyclic and linear polystyrenes, respectively), k_D is negative and becomes increasingly negative with increasing M_w . Expressing k_D in terms of volume fraction units $k_D^* = k_D M / N_A V_h$, where $V_h = 4/3(\pi R_h^3)$, leads to values of k_D^* that are independent of M and are nearly identical for the ring and linear polymers. The average value for all samples is $k_D^* = -2.0 \pm 0.4$, which is in good agreement with the Pyun-Fixman⁴¹ prediction of -2.2. Other theoretical treatments⁴² of k_D predict values from -1 to -2.2; however, several other investigations of linear flexible polymers at Θ -conditions also yielded values of k_D^* in agreement with the Pyun-Fixman prediction.⁴⁰

Values of k_D obtained by Duval et al.³² in the good solvent THF are also shown in Figure 6. The values are all positive and increase with M , indicating that the thermodynamic contribution from the A_2M term is larger than k_f in eq 11. The A_2 values reported by Duval et al. may be used to calculate k_f in the good solvent using eq 11 above. These values, along with those under Θ -conditions measured in this study, are shown as a function of M_w in Figure 7. The k_f values are similar for linear and cyclic polymers in each solvent, so the larger values of k_D observed for the linear polymers in THF are primarily due to the larger A_2 for the linear polymer. For the Θ -solvent cyclohexane, $k_f \propto M_w^{0.5}$ and in the good solvent THF, $k_f \propto M_w^{0.8}$. These exponents are consistent with the expected proportionality of k_f to V_h/M . In both solvents, the k_f values for the cyclic polymers are only slightly smaller than those of the linear polymer of the same molecular weight. This suggests that the proportionality constant in the expression

$$k_f \propto V_h/M$$

is dependent upon chain geometry and is larger for cyclic chains than linear ones, since $V_{h,C}$ is smaller than $V_{h,L}$ by a factor of 0.6.

The ratio $\langle R_g \rangle / \langle R_h \rangle$ in Table I is 1.21 ± 0.05 and 1.00 ± 0.06 for the linear and cyclic chains, respectively. In comparison, theoretical predictions for unperturbed chains are 1.508 and 1.253 for linear and cyclic.²¹ The unperturbed mean square radii of gyration of the linear and cyclic macromolecules measured by SANS agree with the theoretical predictions. Thus, the lower values obtained for the ratios $\langle R_g \rangle / \langle R_h \rangle$ in comparison with the theoretical predictions are due to larger measured hydrodynamic radii than predicted. The experimental value of 1.21 ± 0.05 obtained for the linear polymers is consistent with the value of 1.27 obtained by averaging results from several studies.³⁸ It appears that the hydrodynamic interaction is larger than is estimated as the sum over all interacting pairs, as in the Kirkwood-Riseman theory.⁴⁴ The ratio of $(\langle R_g \rangle / \langle R_h \rangle)_{\text{exptl}}$ obtained experimentally to $(\langle R_g \rangle / \langle R_h \rangle)_{\text{KR}}$ predicted on the basis of Kirkwood-Riseman theory is 0.80 ± 0.04 for both linear and cyclic polymers; the Kirkwood-Riseman theory appears to underestimate the hydrodynamic radius by $\sim 20\%$ for either chain geometry.

4. Concluding Remarks

Cyclic macromolecules differ from linear macromolecules in one important aspect. Cyclic macromolecules can exist in different topological states, which for each macromolecule are fixed during the cyclization reaction. More knotted structures will give rise to an enhanced maximum in the $q^2P(q)$ vs. q plot (see Figure 3) at intermediate angles.⁴⁵ The good agreement found between the experimentally observed scattering and the theoretical prediction based on random flight statistics indicates that most of the cyclic macromolecules are unknotted. However, for the high molecular weight cycles ($M_w > 100\,000$) the fraction of knotted macromolecules may⁴⁵ still be as high as 40%.

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